PB88-104237

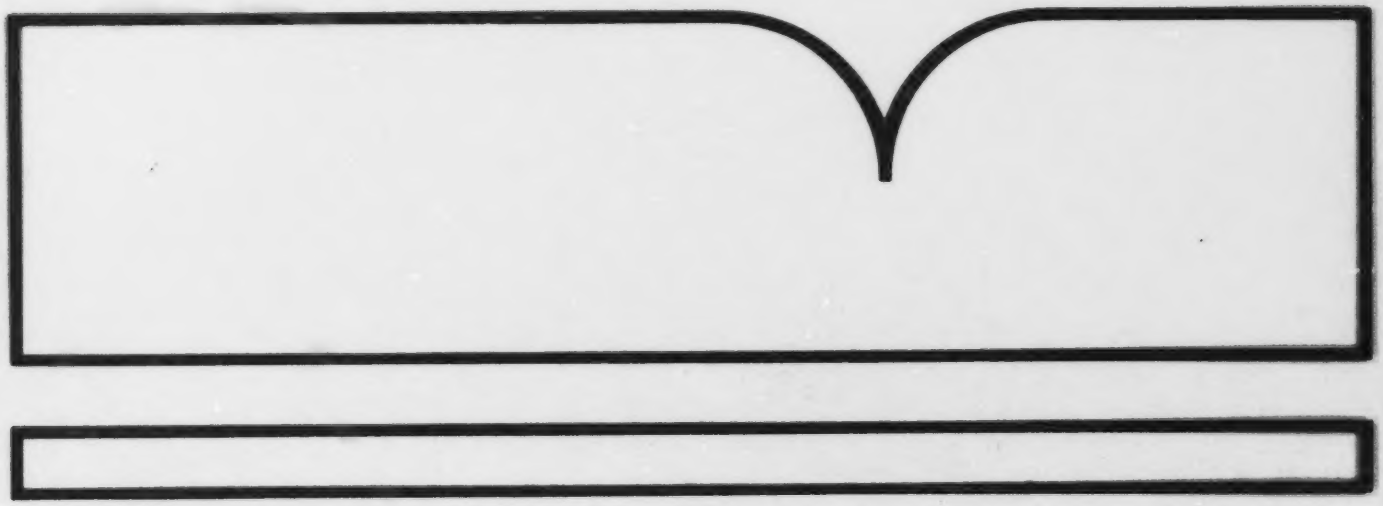
Comparison of Three Methods for Measurement of Atmospheric Nitric Acid and Aerosol Nitrate and Ammonium

Atmospheric Environment Service, Downsview (Ontario)

Prepared for

Environmental Sciences Research Lab.
Research Triangle Park, NC

1985



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1. REPORT NO. EPA/600/J-85/495	2.	3. RE PB88-104237
4. TITLE AND SUBTITLE A COMPARISON OF THREE METHODS FOR MEASUREMENT OF OF ATMOSPHERIC NITRIC ACID AND AEROSOL NITRATE AND AMMONIUM (Journal Version)		5. REPORT DATE 1985 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) K.G. Anlauf, P. Fellin, H.A. Wiebe, H.I. Schiff, G.I. Mackay, R.S. Braman and R. Gilbert		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Atmospheric Environment Service Downsview, Ontario, M3H 5T4 Canada		10. PROGRAM ELEMENT NO. CDTA1D/03-2327 (FY-84) 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, N.C. 27711		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES

REF: Atmospheric Environment, 19(2):325-333, 1985

16. ABSTRACT

Three methods for measuring gaseous ambient nitric acid in the low concentration range 0-15 μg m^{-3} were compared under field conditions in southwestern Ontario during June 1-14, 1982. The methods employed were (1) tunable diode laser absorption, (2) a tungstic acid denuder tube, and (3) a filter pack containing a Teflon-nylon-W41 filter combination operated over 3-hour sampling periods. In general, the three methods measured nitric acid with adequate sensitivity (sub ppb) and they correlated reasonably over the low ambient concentrations considered here. However, there were some notable differences (up to a factor of 2 at night) by the tungstic acid and filter pack methods. These correlated well but again some differences were observed.

During the field comparison, particulate nitrate and ammonium were also measured (0-6 μg m^{-3} range) by the tungstic acid and filter pack methods. These correlated well but again some differences were observed.

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mcg/cu m

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

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U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
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SPRINGFIELD, VA 22161

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 10
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA/600/J-85/495
JOURNAL ARTICLE

Atmospheric Environment Vol. 19, No. 2, pp. 325–333, 1985
Printed in Great Britain.

0004–6981/85 $3.00 + 0.00
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A COMPARISON OF THREE METHODS FOR MEASUREMENT OF ATMOSPHERIC NITRIC ACID AND AEROSOL NITRATE AND AMMONIUM

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(*First received* 16 *April* 1984 *and in final form* 12 *July* 1984)

Abstract—Three methods for measuring gaseous ambient nitric acid in the low concentration range 0–15 $\mu g\,m^{-3}$ were compared under field conditions in Southwestern Ontario during 1–14 June 1982. The methods employed were (1) tunable diode laser absorption, (2) a tungstic acid denuder tube and (3) a filter pack containing a Teflon–nylon-W41 filter combination operated over 3-h sampling periods. In general, the three methods measured nitric acid with adequate sensitivity (sub ppb) and they correlated reasonably over the low ambient concentrations considered here. However, there were some notable differences (up to a factor of 2 at night) by the tungstic acid and filter pack methods. During the field comparison, particulate nitrate and ammonium were also measured (0–6 $\mu g\,m^{-3}$ range) by the tungstic acid and filter pack methods. These correlated well but some differences (less than 20%) were observed in the particulate nitrate measurements. In view of the low concentrations measured and the resultant larger experimental error, specific loss or interfering mechanisms could not be unambiguously identified.

Key word index: Atmospheric, aerosol, particulate, nitric acid, nitrate, measurement, ammonium.

INTRODUCTION

Accurate measurements of atmospheric nitric acid, ammonia and particulate nitrates are of importance to the validation of atmospheric photochemical reaction schemes and to the acid rain issue. Various techniques have been developed and compared. For measurement of nitric acid and particulate nitrate, various combinations of filters and denuder tubes have been commonly used (Stevens, 1979; Fellin *et al.*, 1980; Appel *et al.*, 1981; Shaw *et al.*, 1982; Forrest *et al.*, 1982; Spicer *et al.*, 1982; Goldan *et al.*, 1983; Anlauf *et al.*, 1984). Stevens (1979) has compiled a summary of methods used up to 1979, including the optical long-path Fourier transform infrared method (FTIR) as described by Tuazon *et al.* (1978). This latter method was compared to other methods (Stevens, 1979); however, the detection limit of the FTIR (6 ppb) was not sufficient for meaningful comparisons over most ambient concentrations. Recently, Braman *et al.* (1982) and McClenny *et al.* (1982) have utilized the novel tungstic acid method for measurement of nitric acid, particulate ammonium and gaseous ammonia, and a tunable diode laser absorption method has been successfully applied by Schiff *et al.* (1983) to the measurement of nitric acid and nitrogen oxides at typical ambient concentrations.

An environmental impact study, carried out in southwestern Ontario from 1 to 15 June 1982, provided an excellent opportunity to compare methods for measuring atmospheric nitrogen compounds and at much lower concentrations than previous studies. This paper describes a comparison between the tunable diode laser absorption, tungstic acid and filter methods for measuring the following species: (1) HNO_3 was measured by all three methods, (2) particulate NH_4^+ and NO_3^- were measured by tungstic acid and filter methods and (3) NH_3 was measured solely by the tungstic acid method. The sampling location was on a provincial agricultural experimental farm situated about 4 km east of the town centre of Simcoe (pop. about 11,000) and about 10 km north of Lake Erie. Aside from the town of Simcoe, the surrounding region was totally agricultural in character. A detailed analysis of the ambient concentrations and associated meteorology will be published in a subsequent paper.

Unisearch Associates, Inc. provided the laser based system. This system is particularly appealing since it provides a means for direct, nearly continuous monitoring of HNO_3 without interferences from other

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gases. It uses the principle of infrared absorption which can, intrinsically, be applied to the detection of the majority of atmospheric trace gases. The technique combines the high selectivity of a tunable diode laser spectrometer with the sensitivity of long-path absorption provided by a White cell.

The University of South Florida provided the tungstic acid system and the Atmospheric Environment Service of Environment Canada operated the filter pack system. These two methods are attractive in that they should, in principle, be able to measure gaseous nitric acid and particulate nitrate and ammonium; as an added advantage, the tungstic acid method also measures gaseous ammonia. The simplicity and the low cost of the filter pack method have made it especially attractive for field monitoring measurements. However, the latter two methods yield only integrated concentrations and their accuracy has not, as yet, been fully established.

EXPERIMENTAL

1. *Tunable diode laser absorption method*

The tunable diode laser absorption system (TDLAS) has been described in detail by Schiff *et al.* (1983). Some of the pertinent details are described here.

The diode laser is held in a source assembly maintained to within 0.001 K of the operating temperature which is in the 20–60 K range. Temperature control is provided by the combination of a closed-cycle helium cryocooler, a heater and a ultra-sensitive temperature control system. The current through the laser is supplied by a highly stabilized D.C. current control system and can be changed or modulated by inputs received from a multiple function generator.

The laser radiation is directed by a series of plane mirrors into the 0.8 m base path White cell where the beam makes 28 traverses of the cell to give a total path length of 22.5 m. The exiting beam is directed onto a liquid nitrogen-cooled, mercury–cadmium–telluride detector. The detector output is fed into an oscilloscope for direct viewing and into a lock-in amplifier for processing; a strip chart recorder displays the final signal.

The spectrometer is operated in the frequency modulation (FM) mode. This greatly increases the sensitivity since it eliminates the subtraction of two large signals inherent in the use of direct or amplitude modulated absorption methods. Measurement of the detector output at the first harmonic of the modulation frequency (2f) gives a signal related to the variation in power with frequency rather than the power incident on the detector itself. The amplitude of the 2f signal is proportional to the absorbed power which can be measured with a 10^{-5} sensitivity. For HNO_3, absorptions of this magnitude correspond to mixing ratios in the sub-ppbv range. Since the total laser power is not measured, the spectrometer must be calibrated by introducing known concentrations of a given gas to the air flow.

In operation, a sample of gas is drawn through a three meter long Teflon tube (6 mm o.d., 0.12 mm wall thickness). Particles are removed from the air by a 0.2 μ pore size Teflon filter located at the entrance of the tubing. A Teflon capillary located downstream of the filter maintains the flow into the White cell at 2.5 ℓ min^{-1}. Tests have shown that sample integrity was maintained through the Teflon inlet system (Schiff *et al.*, 1983). The air traverses the inlet line in about 0.2 s while the residence time in the White cell is about 5 s. The flow is monitored with a calibrated mass flowmeter and is measured before each calibration: it is adjusted, when necessary, by a Teflon needle valve situated at the inlet to the White cell. During a measurement, the flowmeter is isolated from the sampling line since tests showed that it affected measurements of HNO_3 in the ppbv range. A MKS Baratron pressure gauge controls a motorized valve which regulates the pressure in the White cell at 25 torr.

The calibration for HNO_3 is by the direct absorption technique. An 11 cm sample cell, containing HNO_3 in air at 25 torr, is placed in the laser beam and the mixing ratio determined by power absorption and the known line strengths. The sensitivity for the White cell is calculated from the path length ratios. Mixtures containing known relative amounts of HNO_3, produced from a diffusion source and introduced upstream of the Teflon filter showed that the 2f signal measured in the White cell was linear with the mixing ratio.

The optical method used for HNO_3 calibration does not account for losses that may occur in the system. However, tests were performed which indicated that sample integrity was maintained through the Teflon inlet tubing and valve.

One data point was obtained approximately every minute. At this acquisition rate, the minimum detectable signal (defined as a signal to noise ratio of 1) in these experiments for nitric acid was 0.35 ppbv. In the concentration range of 0–20 ppb, the accuracy of the measurements was $\pm 20\%$ with a precision $\pm 10\%$. The response time of the instrument to changes in mixing ratio in ambient air of normal humidity was less than 5 min.

For the field comparison study, the TDLAS was mounted in a mobile laboratory which was situated adjacent to the main AES mobile laboratory. During the early part of the study some data was lost due to power and air-conditioning failures. Thereafter, the TDLAS was operated during the day-time of each day for about 12 h with the exception of the 4–5 June and 9–10 June periods when the TDLAS operated continuously for about 36 h; on 6 June, no measurements were made. Calibrations were carried out daily and lasted usually less than one hour. The TDLAS monitored HNO_3 except for the 4–5 June period when NO_2 was monitored.

2. *Tungstic acid method*

Gaseous nitric acid and ammonia, and particulate nitrate and ammonium are preconcentrated from air by chemisorptive reactions on a hollow tube and packed tube combination (Braman *et al.*, 1982; McClenny *et al.*, 1982; Gailey *et al.*, 1983). Gaseous nitric acid and ammonia diffuse to the interior walls of a tungstic acid-coated hollow tube and are collected there by reaction with the tungstic acid. Particles do not diffuse to the walls and pass through the hollow tube to the packed tube where they are collected by impaction. The packed tube consists of tungstic acid coated sand with quartz wool retaining sections. The tungstic acid collects ammonia or nitric acid produced by any particle-to-gas conversion which may occur. Gas collection efficiency is 99% for ammonia and 95% for nitric acid. Particle collection efficiency is approximately 90% as determined by analysis of sequential tubes.

This method was incorporated into an automated analyzer as shown schematically in Fig. 1. It consists of a NO_x detector (with its own vacuum pump and oxygen supply), an air sampling system, a permeation device oven, a sample processing module, control electronics, and a small computer controller. Calibrations were carried out using a Bendix Model 3850-1 permeation system. A wafer-type permeation device provided 60–70 ng min^{-1} of ammonia gas in an air flow of about 2 ℓ min^{-1}.

Analysis of the preconcentrated analytes is by thermal desorption or decomposition. Nitric acid and ammonia are removed from hollow tubes by heating. Nitric acid decomposes to form NO_2, and ammonia is removed as ammonia. These gases, in helium carrier gas, are passed through another cold hollow tube or transfer tube (see Fig. 1) which

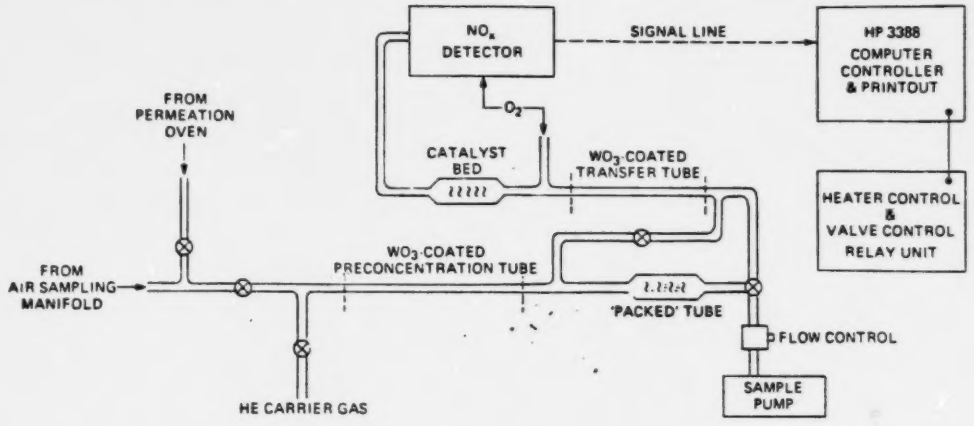

Fig. 1. A schematic of the automated tungstic acid system.

collects the ammonia and passes the nitrogen oxides. Then, ammonia is removed by heating the transfer tube and passing the desorbed ammonia through a catalyst bed (heated gold metal) where it is oxidized to NO. A chemiluminescent NO_x detector senses the NO and NO_2 in the carrier gas stream. Packed tubes are analyzed in the same way as hollow tubes. Nitrates produce NO_2 and NO upon heating while ammonium compounds are converted to ammonia. This analyte mixture is passed through the cold transfer tube and the catalyst bed producing a signal at the detector which is proportional to the nitrate present. Later, the transfer tube is heated producing a signal proportional to the ammonium present.

Previous studies (Braman *et al.*, 1982) have shown that nitrogen dioxide, nitric oxide, HCN, $(CN)_2$, PAN (peroxyacetyl nitrate), volatile organic compounds and small amounts of slightly volatile organic compounds do not interfere and that amines react the same as ammonia.

The automatic analyzer requires approximately 34 min for analysis of a hollow and packed tube pair. Sample times ranged from 15 to 45 min and were adjusted occasionally depending upon the amount of analytes present. The sampling and analysis periods ran sequentially; that is, each sampling period was followed by the analysis period before the next sampling period was initiated. This is important to consider when comparing this method to others that use continuous sampling. Table 1 summarizes the sampling-analysis cycles of the tungstic acid method as used in the present field comparison. Ambient air was sampled at a rate of $1.0\,\ell\,min^{-1}$ through a 1.5 m long Teflon tube (0.6 cm i.d.). Since the detection limit of the chemiluminescence analyzer was 1–2 ng of NH_3 per sample, concentration detection limits were near 0.05 ng $NH_3\,\ell^{-1}$ or 0.1 ng $HNO_3\,\ell^{-1}$ (about 0.04 ppb) depending upon the sample size preconcentrated. The precision of the measurements is in the range 5–10%.

3. *Filter pack*

Figure 2 shows a schematic of the open-face triple filter pack designed at the Atmospheric Environment Service. The parts

Table 1. Sampling-analysis cycle for tungstic acid method

Duration of total cycle (min)	Duration of sampling	
	min	% of total cycle
49	15	30
55	20	36
64	30	47
79	45	57

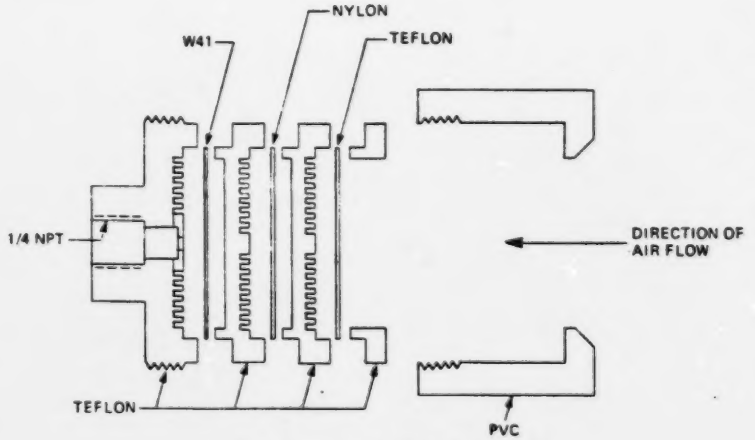

Fig. 2. A schematic of the triple filter pack.

in contact with the filters and the sampled air were made of fluoro-carbon polymer; only the screw cap was made of polyethylene. Three different filters were used in each filter pack. (1) the front one was a 1 μ pore size Teflon filter (with Teflon support mat, Membrana Corp.) for trapping of atmospheric particles. (2) the second or middle one was a 1 μ pore size nylon filter (Membrana Corp.) for trapping of gaseous nitric acid and (3) the third or last one was a Whatman 41 filter, impregnated with an aqueous solution of 10% v/v glycerol and 25% w/v potassium carbonate, for trapping of gaseous sulphur dioxide. No O-rings were used in the system. Instead, the circular filter supports were carefully machined so as to produce a tight fit when hand-assembled. A 0.25 cm shoulder on these supports was sufficient to prevent leakage past the filters. It had been found that O-rings caused leaks around the filters. (This problem had been first encountered for some commercially available filter packs that used O-rings to seal the filter to the filter pack body). The front of each filter support was machined to have concentric ridges for even support of the filter medium, and holes were drilled between them for the air flow.

For each day of sampling, nine complete filter packs were assembled. One was used as a blank and the other eight were each connected via plastic tubing (0.64 cm i.d. Tygon) to a sequential sampler and a pump. All the filter packs (including the blank) were mounted in an open-ended aluminium housing (about 46 cm × 33 cm × 35 cm) attached to the end of a six meter mast. This mast was mounted to the side of the mobile laboratory and could be rotated to ground-level for easy access to the filter packs. The nominal flow rate through each filter pack was 30 ℓ min^{-1} and was continuously measured by a Hastings mass flowmeter. The sampling time per filter pack was 3 h and the volume of air sampled was 4–6 m^3.

Filter packs were loaded and unloaded each day in the field. The sampled filters were individually stored in plastic Petri dishes and the analysis began in the laboratory immediately after the field study had been completed. The extraction procedure was as follows: (1) Teflon filters, each filter was placed in a 50 ml polyethylene bottle and 15 ml of de-ionized water was added. A glass rod was used to submerge the filter during a 30-min ultrasonic extraction. (2) Nylon filters, each filter was placed into a 50 ml polyethylene bottle along with 15 ml of 0.01 mol ℓ^{-1} NaOH solution; this was manually shaken and then left standing for analysis. (3) W41 filters, each filter was extracted with 15 ml of 0.03% H_2O_2 solution in a 50 ml polyethylene bottle.

Analysis of the Teflon and nylon filter extracts was done by ion-chromatography using an automated Dionex Model 10 system. The W41 filters were analyzed for sulphate by the Thorin colorimetric method using a Technicon Autoanalyzer system. It was found that the nylon filter retained 5–10% of the ambient sulphur dioxide as sulphate and, hence, all the W41 derived sulphate concentrations were corrected for this effect. The detection limits of the measured species were limited by their field blanks. For HNO_3, the detection limit was about 0.2 ppb for a sample volume of 5 m^3 and based on the average filter blank plus two times the mean standard deviation of the filter blanks. Table 2 summarizes the averages and mean standard deviations of the field filter blanks. (Note that the blank values are expressed as μg per filter). All reported concentrations were corrected by these average field blanks. From other field studies, the accuracy of this method is thought to be better than ± 20% and a precision better than ± 8% (Fellin *et al.*, 1980; Anlauf *et al.*, 1984).

RESULTS

1. *Nitric acid measurement*

Figure 3 shows the nitric acid concentrations as measured by the three methods during the comparison period. The filter pack and laser results are plotted as 3-h averages. For the tungstic acid method, since the sampling times were only 15–45 min in duration, points are used to represent these results. From Fig. 3, it can be seen that the three methods correlate well qualitatively and that they measure nitric acid with adequate sensitivity in the low ppb range (1 ppb HNO_3 = 2.6 μg m^{-3} at 760 torr, 20 C). Also, as the field study progressed, the daily maximum concentrations as measured by the tungstic acid method came into closer agreement with the other two methods. At night-time, the tungstic acid method yielded, with few exceptions, larger concentrations than the filter pack method.

Figure 4 shows the individual laser-derived concentrations (about one per min) and those for the tungstic acid and filter pack methods for the period 9–10 June; the latter two are shown as integrated averages for their respective sampling periods. The great detail on ambient nitric acid concentrations available by the laser technique is readily apparent in Fig. 4. For example, the maximum concentration as measured by the laser on 9 June was about 21 μg m^{-3}, whereas the filter pack yielded about 9.1 μg m^{-3} and the tungstic acid about 5.1 μg m^{-3}. Furthermore, the laser is able to resolve the rapid fluctuations in HNO_3 concentration. This type of measurement is especially useful for atmospheric modelling purposes.

A least-square linear correlation was performed on each pair of the three methods. Figures 5–7 show the correlation graphs and Table 3 summarizes the statistical results. On the figures, the open symbols denote daytime (8:00–20:00 EDT) measurements and the closed symbols denote night-time (20:00–8:00 EDT) measurements. The dashed line of slope 1.0 represents 1:1 correspondence between methods.

For the laser-filter pack and laser-tungstic acid correlations, the laser data was first averaged over the filter pack and tungstic acid sampling periods and then correlated. These two particular correlations are shown in Figs 5 and 6, respectively; the vertical bars associated with every data point indicate the standard deviation from the mean of the laser-derived concen-

Table 2. Field blank values (μg filter^{-1}) for 47 mm dia. filters

	Teflon			Nylon		Whatman 41
	NH_4^+	NO_3^-	SO_4^{2-}	NO_3^-	SO_4^{2-}	SO_4^{2-}
Average	0.57	1.11	1.35	1.85	0.71	12.0
Std. deviation	0.32	0.65	0.72	0.23	0.45	6.0
No. of samples	13	13	13	13	13	12

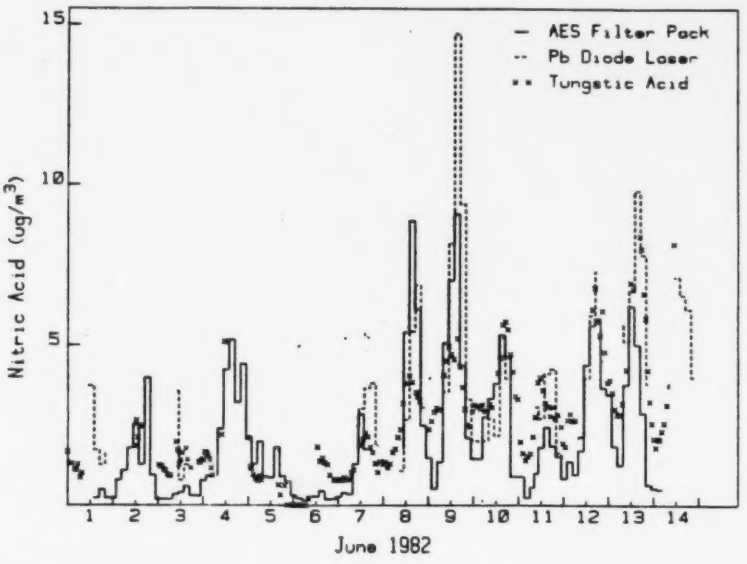

Fig. 3. Nitric acid concentrations as measured by the three methods for the period 1–14 June 1982.

trations within the averaging period. From Table 3, the corresponding correlation coefficients are 0.74 and 0.52, and the slopes of the regression lines are 0.96 and 0.99, respectively. A good quantitative measure of the scatter about the regression line is the standard error of estimate of y on x, $s_{y.x}$. Two lines, drawn parallel to the regression line and separated vertically by $\pm s_{y.x}$ from it, would include about 68 % of the sample points. For the two correlations under consideration, this is 2.1 and 2.7 $\mu g\,m^{-3}$, respectively (see Table 3). A significant

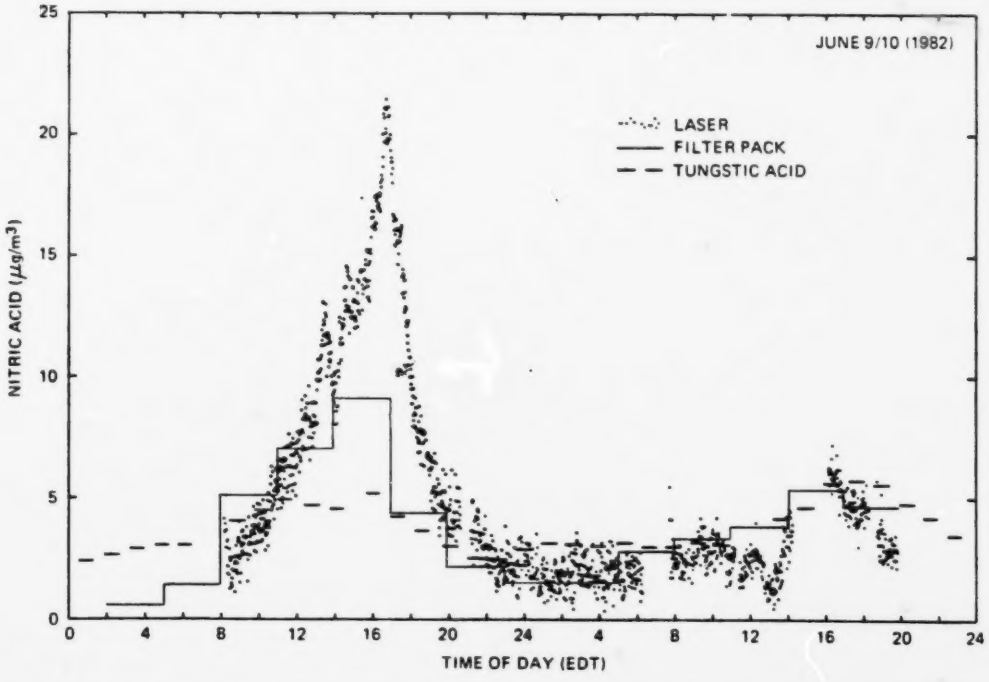

Fig. 4. Nitric acid concentrations as measured by the three methods on 9–10 June 1982; the dots represent individual laser measurements (about one per minute); the horizontal bars represent the filter pack and tungstic acid measurements, the length of the bar corresponds to the duration of sampling.

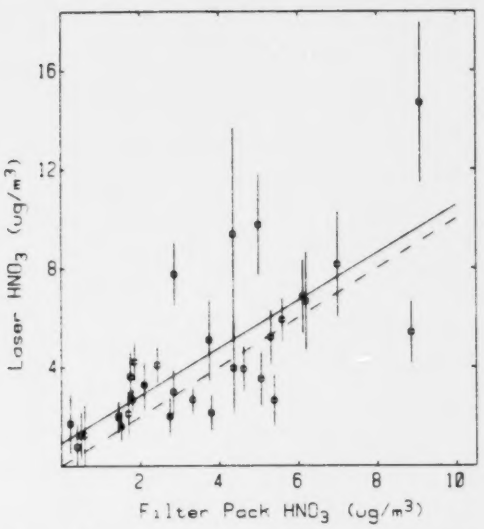

Fig. 5. Comparison of laser and filter pack nitric acid measurements: (--) = 1:1 line; (——) = regression line; (□) = daytime (8:00–20:00 EDT) and (■) = night-time (20:00–8:00 EDT) measurements.

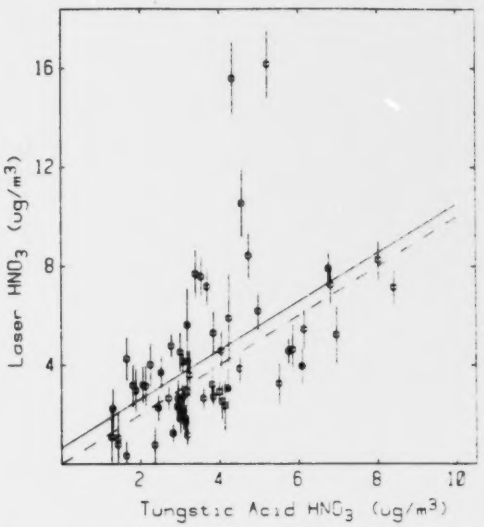

Fig. 6. Comparison of laser and tungstic acid nitric acid measurements: measurements: (--) = 1:1 line; (——) = regression line; (□) = day-time (8:00–20:00 EDT) and (■) = night-time (20:00–8:00 EDT) measurements.

amount of this scatter is due to data outliers. In general, it can be said that the laser method reported larger nitric acid concentrations than the other two methods; this difference in averaged concentrations was in the range 15–20%.

For the tungstic acid-filter pack correlation, the tungstic acid data were averaged over the 3-h filter pack sampling periods. From Table 1, however, it must be noted that the tungstic acid measurements encompassed only 30–57% of any given 3-h filter pack sampling period. This will undoubtedly contribute additional scatter to the correlation of this particular pair of methods since the nitric acid concentration can fluctuate rapidly within this period as seen in Fig. 4. The statistical results are summarized in Table 3, and Fig. 7 shows the correlation plot. In this figure, each vertical line centred on a data point shows the spread in tungstic acid concentrations that were averaged in any one filter pack period. Considering all the measurements common to both methods, the calculated correlation coefficient is 0.73, the slope of the regression line is 0.61 and the standard error of estimate, $s_{y.x}$, is 1.24 $\mu g\,m^{-3}$. Part of the scatter is due to the large

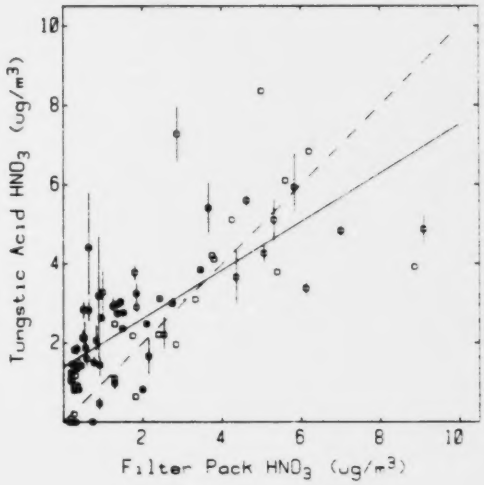

Fig. 7. Comparison of tungstic acid and filter pack nitric acid measurements: (--) = 1:1 line; (——) = regression line; (□) = day-time (8:00–20:00 EDT) and (■) = night-time (20:00–8:00 EDT) measurements.

Table 3. Statistics of the regression calculation on nitric acid concentration ($\mu g\,m^{-3}$)

y variable	Laser	Laser	Tungstic acid		
x variable	Filter pack	Tungstic acid	Filter pack		
Data set	All	All	All	Day	Night
Average, y	4.37	4.32	2.72	3.36	2.06
Average, x	3.57	3.71	2.16	3.19	1.09
Correlation coefficient	0.74	0.52	0.73	0.71	0.63
Slope of correlation line	0.96	0.99	0.61	0.57	0.89
y-intercept	0.94	0.66	1.40	1.52	1.08
No. of samples	32	60	75	38	37
Standard error of estimate, $s_{y.x}$	2.09	2.65	1.24	1.43	1.00

number of points at very low concentrations, $< 2\,\mu g\,m^{-3}$, and also to some outliers at large concentrations. Overall, the tungstic acid method measured higher nitric acid concentrations than the filter pack; from Table 3, this difference was about 20% when all the data was averaged but was only 5% for day-time measurements. However, there was a striking difference between the two methods for night-time (20:00–8:00 EDT) measurements. During this time, the nitric acid concentration was invariably low and the filter pack method consistently yielded the lowest concentrations, about a factor of two lower than the tungstic acid method.

Only on one occasion, 9–10 June, was the laser operated throughout the night to measure nitric acid. For this particular night (20:00–8:00 EDT), the average HNO_3 concentrations were $1.94\,\mu g\,m^{-3}$ for the filter pack, $2.32\,\mu g\,m^{-3}$ for the laser and $2.90\,\mu g\,m^{-3}$ for the tungstic acid method. This is to be contrasted with daytime measurements when the laser method yielded HNO_3 concentrations about 20–25% larger than either of the other two methods. Hence, it seems that at night, the tungstic acid method measures HNO_3 concentrations appreciably larger than those from the laser or filter pack.

It is to be noted that our comparison was for low HNO_3 concentrations in the range $0–16\,\mu g\,m^{-3}$. Within this range, our measurement differences compare well with those of other similar studies (Forrest *et al.*, 1982; Spicer *et al.*, 1982) made at much larger ambient concentrations.

2. *Particulate ammonium and nitrate measurements*

Table 4 shows the correlation statistics and average concentrations as measured by the tungstic acid and filter pack methods. Figures 8 and 9 show the corresponding correlation plots where, as before, the closed symbols denote night-time (20:00–8:00 EDT) measurements and the open symbols denote those for daytime (8:00–20:00 EDT).

Generally, the two methods showed a good correlation, $r = 0.89$ for NH_4^+ and 0.85 for NO_3^-; however, this was accompanied by an appreciable amount of scatter—the standard error of estimate, $s_{y,x}$, was $0.74\,\mu g\,m^{-3}$ for NH_4^+ and $0.67\,\mu g\,m^{-3}$ for NO_3^-. There were no significant differences between the two methods in measuring particulate ammonium during daytime or night-time. For particulate nitrate, how-

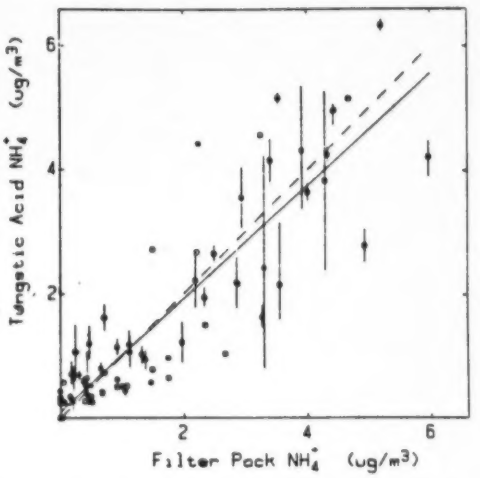

Fig. 8. Comparison of tungstic acid and filter pack particulate ammonium measurements: (– –) = 1:1 line; (——) = regression line; (□) = daytime (8:00–20:00 EDT) and (■) = night-time (20:00–8:00 EDT) measurements.

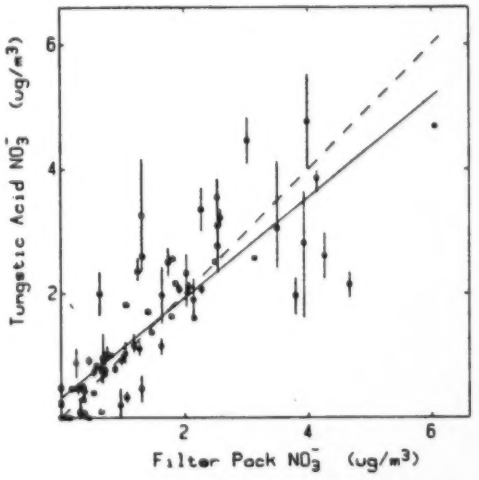

Fig. 9. Comparison of tungstic acid and filter pack particulate nitrate measurements: (– –) = 1:1 line; (——) = regression line; (□) = daytime (8:00–20:00 EDT) and (■) = night-time (20:00–8:00 EDT) measurements.

Table 4. Statistics of the regression calculation on particulate NH_4^+ and NO_3^- concentrations ($\mu g\,m^{-3}$)

Species	NH_4^+			NO_3^-		
Data set	Day	Night	All	Day	Night	All
Mean, y (= Tungstic acid)	1.77	1.40	1.59	1.44	1.51	1.47
Mean, x (= Filter pack)	1.85	1.41	1.63	1.15	1.72	1.43
Correlation coefficient	0.88	0.90	0.89	0.87	0.88	0.85
Slope of correlation line	0.88	0.96	0.91	1.09	0.76	0.81
y-intercept	0.15	0.05	0.11	0.19	0.20	0.32
No. of samples	38	37	75	38	37	75
Std. error of estimate, $s_{y,x}$	0.83	0.64	0.74	0.56	0.67	0.67

ever, the filter pack method measured about 20% lower than the tungstic acid method during daytime; at night, the opposite trend was observed with the tungstic acid method being lower by about 12%.

3. Differences in nitric acid and particulate nitrate measurements

Several research groups (Appel *et al.*, 1981; Shaw *et al.*, 1982; Forrest *et al.*, 1982; Spicer *et al.*, 1982) have apparently observed appreciable particulate nitrate losses from Teflon pre-filters and corresponding nitric acid gains on the back-up nitric acid absorbing filters. Generally, these observations were made under higher ambient temperatures and lower relative humidities than those encountered during this field comparison period. With few exceptions, the daytime (8:00–20:00 EDT) temperature range was 15–25°C and the corresponding relative humidity range was 60–80%; the night-time (20:00–8:00 EDT) ranges were 7–15°C and 80–100%, respectively. Under these conditions, the particulate nitrate losses would be expected to be appreciably less because there is a strong positive temperature dependence of the ammonium nitrate dissociation constant, and the relative humidity was frequently above that needed for deliquescence of the particulate ammonium nitrate (Stelson and Seinfeld, 1982). For our temperature range, the relative humidity of deliquescence was in the range 60–75%.

The differences observed between the filter pack and tungstic acid methods might, in part, be attributed to nitrate losses from the Teflon pre-filter of the filter pack method. As shown in Table 4, during daytime, the filter pack average particulate nitrate concentration was about 20% lower than the tungstic acid method. If nitrate losses on the Teflon pre-filter were important and the source of this difference, then the filter pack average nitric acid concentration should have been larger than the tungstic acid method by 10%—yet it was lower by about 5%; this is within experimental error. In contrast, during night-time, the filter pack method measured nitric acid about a factor of two lower than the tungstic acid method, yet the comparable particulate nitrate difference was only 12%. Qualitatively, this night-time difference might be attributed to the effect of retention of nitric acid on the particulate matter collected on the front filter (Appel *et al.*, 1980). In particular, Forrest *et al.* (1982) point to this effect as being a dominant error source in filter methodologies during night-time sampling. However, quantitatively, the nitric acid deficit is much larger than the small increase in particulate nitrate. Furthermore, maximum particulate loadings were less than 150 μg per filter during daytime (average loading of 40 μg per filter) and less than 100 μg per filter during night-time (average loading of 30 μg per filter). At these maximum loadings, Appel *et al.* (1980) have measured nitric acid retention of 4–8%. Since the average loading was in the range 30–40 μg per filter, the effect of this interference would seem to be within the experimental uncertainties. Hence, the observed night-time difference cannot be explained solely on the basis of the two above-mentioned interfering processes. The results do suggest, though, that the net effect of evaporative particulate nitrate loss and nitric acid retention on pre-filter particulate matter is, on average, probably less than 20% under the conditions of this comparison study.

Consideration was given to the possibility that ammonium nitrate particles trapped on the 0.2 μ Teflon filter at the inlet of the sampling line to the laser system might decompose and be detected as HNO_3. However, steady-state smog chamber tests done elsewhere established that this did not occur. In these tests, chamber air (relative humidity about 50%) containing HNO_3, NH_3 and NH_4NO_3 particles was sampled. No differences in HNO_3 concentrations were observed whether or not the Teflon filter was in the sampling line. Moreover, when a nylon filter was inserted before the Teflon filter, the measured HNO_3 concentration dropped to zero. In addition, no HNO_3 was observed when HNO_3-free cylinder air was passed through the Teflon filter loaded with NH_4NO_3. These tests showed that the higher HNO_3 measurements obtained with the laser system cannot be attributed to NH_4NO_3 decomposition.

Previous extensive laboratory tests by the Atmospheric Environment Service (Fellin *et al.*, 1980) have not shown humidity effects to be important. A detailed comparison of the filter pack nitric acid measurements with concurrent relative humidity and absolute water content measurements did not yield a self-consistent explanation for the observed night-time difference in the methods. Since there is, as yet, no conclusive explanation for this difference, further tests have been initiated to elucidate the cause.

CONCLUSIONS

The three methods successfully measured gaseous nitric acid in the low concentration range 0–15 $\mu g\,m^{-3}$. Over the comparison period, for day-time measurements (8:00–20:00 EDT) of nitric acid, the filter pack and tungstic acid methods measured concentrations about 16% lower, on average, than the laser method. For night-time measurements (20:00–8:00 EDT) of nitric acid (concentration less than 3 $\mu g\,m^{-3}$) the tungstic acid results were about a factor of two larger than those for the filter pack method.

For measurement of particulate ammonium, the tungstic acid and filter pack methods correlated very well. For particulate nitrate measurement, the correlation coefficient was 0.85 and the slope of the regression line was 0.81; however, there were some day–night differences. During the day-time the filter pack was about 20% lower than the tungstic acid method, and during night-time the latter was about 12% lower than the filter pack.

Undoubtedly a large source of uncertainty in the

measurements can be attributed to the low concentrations being measured. However, the observed nighttime nitric acid discrepancy (filter pack vs tungstic acid method) could not be attributed solely to particulate nitrate evaporative losses or retention of nitric acid on the collected material of the pre-filter; the major source of this difference is yet to be identified. Some of the observed differences do suggest, though, that for the conditions of this study, the combination of these two interfering effects is less than 20%.

Further detailed laboratory comparisons and calibrations under controlled conditions are in progress in order to resolve some of the differences observed during the field comparison.

Acknowledgements—We wish to thank the Coordinating Research Council for support in developing TDLAS and we are grateful to T. Iguchi for some of the data abstraction and presentation.

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